Supporting Information

Discovery of Fe_2P-type $Ti(Zr/Hf)_2O_6$ Photocatalysts toward Water Splitting

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1. The crystallographic information (in *.cif* format) for $TiZr_2O_6$

```
# CRYSTAL DATA
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data_VESTA_phase_1
_pd_phase_name                         'TiZr2O6'
_cell_length_a                         5.59950
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_symmetry_Int_Tables_number            189

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   '-x+y, -x, z'
   'x, y, -z'
   '-y, x-y, -z'
   '-x+y, -x, -z'
   'y, x, -z'
   'x-y, -y, -z'
   '-x, -x+y, -z'
   'y, x, z'
   'x-y, -y, z'
   '-x, -x+y, z'

loop_
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   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
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   O4     1.0    0.597320    0.000000    0.500000    Uiso    0.012670 O
   Ti1    1.0   -0.000000   -0.000000    0.500000    Uiso    0.012670 Ti
   Zr1    1.0    0.666667    0.333333    0.000000    Uiso    0.012670 Zr
```

2. The crystallographic information (in *.cif* format) for $TiHf_2O_6$

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loop_
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   _atom_site_type_symbol
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   O4     1.0    0.406850    0.000000   -0.000000    Uiso    0.012670 O
   Ti1    1.0   -0.000000    0.000000    0.000000    Uiso    0.012670 Ti
   Hf1    1.0    0.666667    0.333333    0.500000    Uiso    0.012670 Hf
```

3. The elastic constants and modulus of Ti $(Zr/Hf)_2O_6$

Based on the energy-strain relations, the independent elastic constants of $Ti(Zr/Hf)_2O_6$ at the zero-pressure are calculated and listed in Table 1s. It is clear that the calculated elastic constants of $Ti(Zr/Hf)_2O_6$ fulfill the mechanical stability criteria: $C_{44} > 0$, $C_{11} > |C_{12}|$, and $(C_{11} + C_{12})C_{33} > 2C^2_{12}$.

4. The phonon dispersion curves at 0 GPa of Fe_2P-type ZrO_2 and HfO_2

In Fig. 1s_a, no imaginary phonon frequency is observed in Fe_2P-type ZrO_2 at 0 GPa, indicating its dynamical instability at ambient conditions. However, in Fe_2P-type HfO_2 (Fig. 1s_b), an acoustic phonon branch is found negative. The dynamical stability of Fe_2P-type at ambient conditions need to be further investigated by both theoretical and experimental studies.

5. HSE band structures at 0 GPa of Fe_2P-type ZrO_2 and HfO_2

HSE obtained band structures of ZrO_2 and HfO_2 are shown in Fig. 2s. The present calculations give bandgaps of 2.64 eV and 3.00 eV for Fe_2P-type ZrO_2 and HfO_2, respectively. The ionicity for the Fe_2P-type compounds is listed in Table 2s. The bandgap of Fe_2P-type IVa-oxides is found to be wider and wider with the increase of the ioncity.

Table S1. The independent elastic constants and modulus (bulk modulus *B*, shear modulus *G*, Young's modulus *E*, and Poisson's ratio *v*) of $Ti(Zr/Hf)_2O_6$. All elastic parameters except *v* are in GPa.

	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	*B*	*G*	*E*	*v*	*B/G*
$TiZr_2O_6$	458	424	124	124	250	175	281	115	305	0.32	2.43
$TiHf_2O_6$	475	442	132	102	269	177	291	119	314	0.32	2.45

Table S2. The ionicity and HSE bandgap (eV) of Fe_2P-type IVa-oxides.

	TiO_2	$TiZr_2O_6$	ZrO_2	$TiHf_2O_6$	HfO_2
Ionicity	39%	42%	44%	45%	48%
HSE Bandgap	2.00	2.29	2.64	2.65	3.00

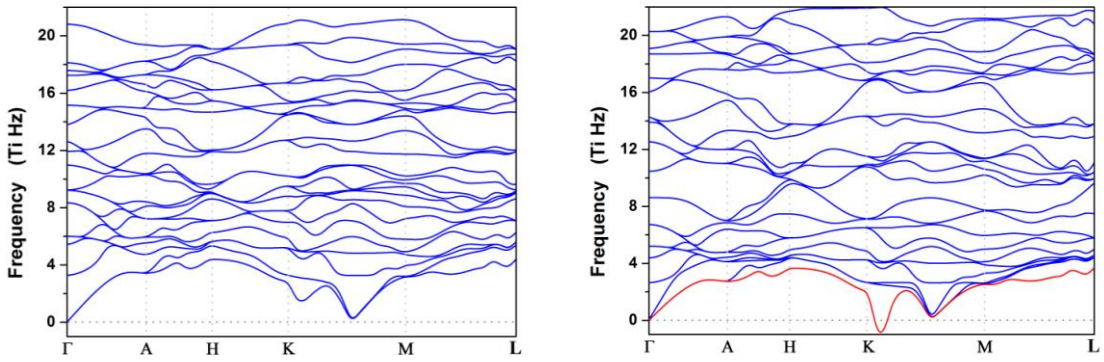

Figure S1. Phonon dispersion curves for Fe_2P-type ZrO_2 (a) and HfO_2 (b) at 0GPa

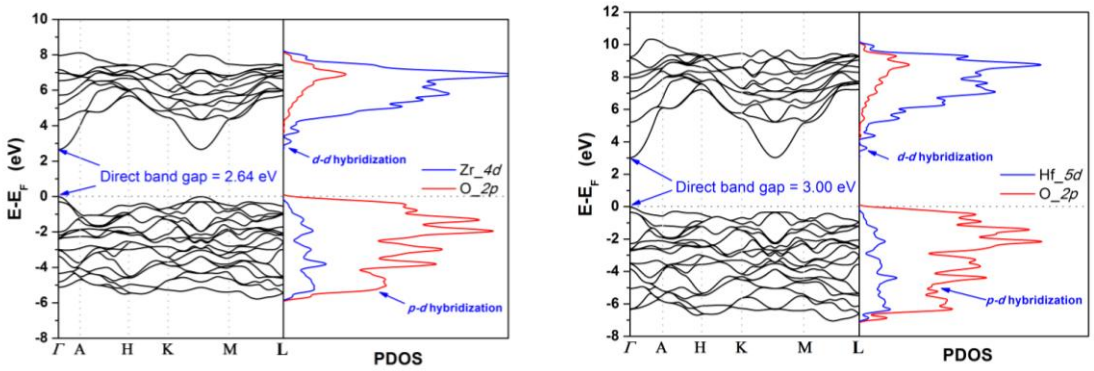

Figure S2. HSE band structure of Fe_2P-type ZrO_2 (a) and HfO_2 (b) at 0 GPa